RI 9321

REPORT OF INVESTIGATIONS/1990

Infrared Spectroscopic Study of the Flocculation of Zinc and Copper Precipitates

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1910 ★ 80 YEARS ★ 1990

BUREAU OF MINES

UNITED STATES DEPARTMENT OF THE INTERIOR

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Manuel Lujan, Jr., Secretary

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T S Ary, Director

This report is based upon work done under an agreement between the University of Alabama and the Bureau of Mines.

Library of Congress Cataloging in Publication Data:

Susko, Frank J.
Infrared spectroscopic study of the flocculation of zinc and copper precipitates / by Frank J. Susko and B. J. Scheiner.

p. cm. – (Report of investigations; 9321)

Includes bibliographical references: (p. 5)

Supt. of Docs. no.: I 28.23:9321.

1. Flocculation. 2. Infrared spectroscopy. 3. Precipitation (chemistry). I. Scheiner, Bernard J. II. Title. III. Series: Report of investigations (United States. Bureau of Mines); 9321.

TN23.U43 [QD547] 622 s–dc20 [622'.7] 90-2102 CIP

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	h	hour
cm	centimeter	min	minute
cm^{-1}	wavenumber	mL	milliliter
g	gram	pct	percent
g/L	gram per liter		

INFRARED SPECTROSCOPIC STUDY OF THE FLOCCULATION OF ZINC AND COPPER PRECIPITATES

By Frank J. Susko[1] and B. J. Scheiner[2]

ABSTRACT

The U.S. Bureau of Mines is developing a process for removing metals from mining and mineral processing waste streams by precipitation. The precipitation process is accelerated by flocculation when a high molecular weight polymer is added. Infrared (IR) studies were performed on zinc hydroxide [$Zn(OH)_2$], copper hydroxide [$Cu(OH)_2$], and zinc sulfide (ZnS) flocculated with both nonionic and anionic polyacrylamide (PAM) and polyethylene oxide (PEO). The IR data were compared with general trends in the performance of the polymers observed during flocculation. These studies will help to understand the bonding between the precipitate and polymer and indicate the effectiveness of a flocculant for dewatering.

Two types of bands showed up on the IR spectra; one type described the interlayer water of the flocs, the other described the organic bonds of the polymers. A general decrease in the areas of the three water bands, hydroxyl (O-H) stretching (3,200-3,500 cm^{-1}), water bending (1,610-1,630 cm^{-1}), and torsional oscillations (600-700 cm^{-1}), indicate interlayer water being driven off, which is a favorable condition in flocculation. Shifts in the O-H stretching band indicate water bridging between the precipitate and polymer. Shifts in the amine (N-H) deformation, carbon-nitrogen (C-N) stretch band (1,600-1,610 cm^{-1}) indicate the amine group of the PAM is involved in the bonding. Evidence suggests that ether oxygen of PEO is also involved in the bonding process.

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INTRODUCTION

Mining and mineral processing operations often produce waste streams that contain dissolved metal ions. These waste stream metal ions pose an environmental threat and are also a potential source of valuable metals. The usual practice of dealing with these waste streams is to precipitate the metal ions with lime. However, the resulting sludge retains large amounts of water and filters poorly. The use of flocculants in the mining and mineral industry is well documented, but the application of flocculating agents for metal hydroxide sludges has received little attention. As a result, the U.S. Bureau of Mines has been investigating the removal of metals from mining and mineral processing waste streams. The study involved the precipitation of metals such as zinc and copper with hydroxyl or sulfide ion. The resulting precipitate contained large quantities of water and settled slowly. Flocculation of the precipitates with high molecular weight polymer accelerated the settling. In previous research, the Bureau developed a flocculation technique for a variety of mineral slurries using PEO as the flocculating agent (*1*).[3] As part of the research, IR spectroscopy was used to determine the type of association between the polymer and montmorillonite clays (*2*). It was determined that characteristic shifts occur in the frequency bands of the IR spectra when an organic molecule is adsorbed onto the surface of a clay mineral. Interpreting the shifts in the frequency bands can give insight into the mode of attachment between the polymer and clay surface. In this report, IR spectroscopy was applied to the study of zinc and copper precipitates treated with PAM and PEO. The IR spectra of the zinc and copper precipitates with and without addition of various polymers were studied. The spectra was compared with general trends in the polymers' performance as flocculating agents. These studies will help to understand the bonding between the precipitate and polymer and determine the effectiveness of a flocculant for dewatering.

BACKGROUND

For IR spectra obtained from flocculating mineral slurries, the analysis of the coordinated water bands before and after flocculation are of major interest. Several articles described the possible spectral bands for water associated with mineral slurries (*2-7*). Two of these types of bands are the O-H stretching, appearing between 3,200 and 3,500 cm^{-1}, and the water bending, appearing between 1,610 and 1,630 cm^{-1} (*3*). These bands are due to water molecules coordinated in the crystal lattice. The area of the water bending band is related to the amount of water present in the interlayer region (*2-3*). It has been reported that heating the mineral removes the interlayer water and has been illustrated on an IR spectra by a decrease in the area of the water bending band (*4*). It has also been reported that a shift in the water bending band to a higher wave number occurs upon addition of polymer. The shift was due to the polymer's influence on the water of hydration, indicating the polymer's interaction with the cation of montmorillonite through a water bridge (*2*). Another frequency band shift involving the O-H stretching where an increase in hydrogen bonding produces a shift in the O-H stretching band to a lower frequency has been reported (*5*). A third water band occurs around 600 cm^{-1} and has been reported as the torsional oscillations band (*3, 6-7*). This band is due to the hindered rotations of the water molecule locked in the lattice structure resulting in oscillations of the entire molecule.

Several articles have also dealt with vibrational assignments of metal-organic bonds such as the metal-amine frequency band assignment in a copper-urea complex (*7-9*). The N-H bending and C-N stretching frequencies of urea shifted to a lower wave number upon complexation with copper. The frequency shifts were due to the complexation of copper through the nitrogen of the amine group. Other investigations showed that when copper is reacted with acetylacetone, a complex is formed with carbonyl groups and a carbonyl band shift from 1,610 to 1,580 cm^{-1} is observed (*8*).

Previous research conducted by the Bureau has shown that when PEO is reacted with montmorillonite, certain shifts in the IR spectra are observed. These shifts were due to the adsorptions of PEO onto montmorillonite clays via the exchange ion of the clay. The methylene (CH_2) symmetric-antisymmetric band of PEO at 2,880 cm^{-1} shifted to a higher wave number upon adsorption. The hydrophobic nature of CH_2 lead to the adsorption onto the magnesium ion of magnesium exchanged montmorillonite (*2*). The ether group of PEO could be considered a weak proton acceptor and was another possible site of adsorption (*9*).

EXPERIMENTAL PROCEDURE

Solutions of zinc chloride and copper chloride with metal concentrations of 2.0 g/L were treated with stoichiometric amounts of calcium hydroxide or sodium sulfide. The precipitants were added all at once, stirred for 5 min, then allowed to settle for 5 min. The resulting precipitate was flocculated with nonionic PAM, anionic PAM (34 pct hydrolyzed) or PEO at concentrations of 0.075 and 0.60 g of polymer per liter of solution. The polymer was added slowly and mixed for 5 min. A control test was also run for both metals by adding deionized water instead of polymer. The molecular structures of the three polymers are illustrated in figure 1. The reagents used were analytical grade and were obtained from various commercial sources.

The following procedure, used to prepare the samples for IR analysis, was similar to one developed for ion-exchanged montmorillonite treated with PEO (*2*). A 0.1-mL sample from each of the untreated and

[3]Italic numbers in parentheses refer to items in the list of references at the end of this report.

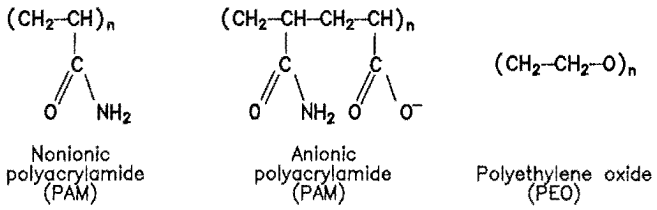

Figure 1.–Molecular structures of polymers used as flocculants.

polymer-treated precipitate suspensions was dried overnight on a silver chloride plate (2.5 by 1.3 by 0.05 cm) in a desiccator over calcium sulfate at atmospheric pressure and room temperature. A 0.1-mL sample of each of the polymers was prepared in the same manner. Each of the dried samples was scanned using a Perkin Elmer[4] 684 IR spectrophotometer. The instrument was run at medium slit width with a 5 min scan time and in percent transmission mode. Resolution was set at 1 cm^{-1} and an average of three scans were taken for each sample. The samples were automatically scanned from 4,000 to 400 cm^{-1} using a Perkin Elmer 3600 data station. Noise was removed from the resulting spectra using a five-point smoothing routine provided with the data station. The location and areas of the frequency bands were determined using software also provided with the data station.

[4]Reference to specific products does not imply endorsement by the U.S. Bureau of Mines.

RESULTS AND DISCUSSION

Two types of bands showed up on the IR spectra. One type described coordinated water of the flocs; the other described the organic groups of the polymers.

Three frequency bands describing interlayer water appeared on the spectra. They were the O-H stretching (which occurred at approximately 3,200-3,400 cm^{-1}), water bending vibration (1,610-1,625 cm^{-1}), and torsional oscillations (600-700 cm^{-1}). To study these bands, the spectra of the metal precipitates, shown in figures 2 and 3, were compared with the spectra of the precipitates treated with the different polymers.

The O-H stretching band frequencies from the spectra of the three flocculated precipitates are listed in table 1. In each case, the band shifted to a lower frequency upon addition of any of the polymers. This shift is an indication of an increase in hydrogen bonding (*5*). The increase in hydrogen bonding indicates greater stability of the precipitate and indicates the involvement of water bridge between the precipitate and the polymer (*5*).

Table 1.–Hydroxyl stretching band frequencies for metal precipitates treated with polymer, wavenumber

Polymer	$Zn(OH)_2$	$Cu(OH)_2$	ZnS
Control[1]	3,443	3,441	3,523
Nonionic PAM ..	3,411	3,336	3,507
Anionic PAM ...	3,427	3,336	3,512
PEO	3,432	3,336	3,507

[1]Precipitate without polymer.

The water bending band frequencies from the spectra of zinc hydroxide, copper hydroxide, and zinc sulfide are shown in table 2. The results show that there were no band shifts in either the zinc hydroxide or the copper hydroxide tests. The spectra of the zinc sulfide showed a small shift in the water bending vibration for each of the polymers tested. Webb (*2*) reported this type of shift is due to water molecules acting as a bridge between the exchange ion of montmorillonite and the polymer PEO. The shift in the case of zinc sulfide is most likely due to water molecules acting as a bridge between the metal specie of the precipitate and the polymer. The reason for not observing a shift for the copper and zinc hydroxide can be explained by the spectra shown in figure 2. The hydroxyl ions of the metal precipitates have a band peak at 1,627 cm^{-1} that would mask the band shift.

Table 2.–Water bending band frequencies for metal precipitates treated with polymer, wavenumber

Polymer	$Zn(OH)_2$	$Cu(OH)_2$	ZnS
Control[1]	1,627	1,627	1,612
Nonionic PAM ..	1,627	1,627	1,616
Anionic PAM ...	1,627	1,627	1,616
PEO	1,627	1,627	1,616

[1]Precipitate without polymer.

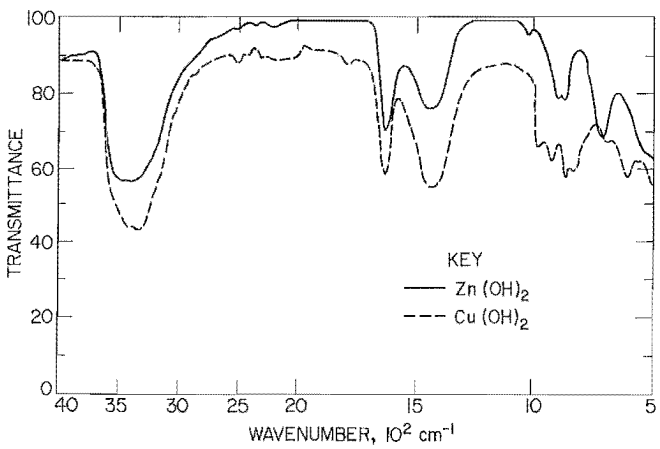

Figure 2.–IR spectra of $Zn(OH)_2$ and $Cu(OH)_2$.

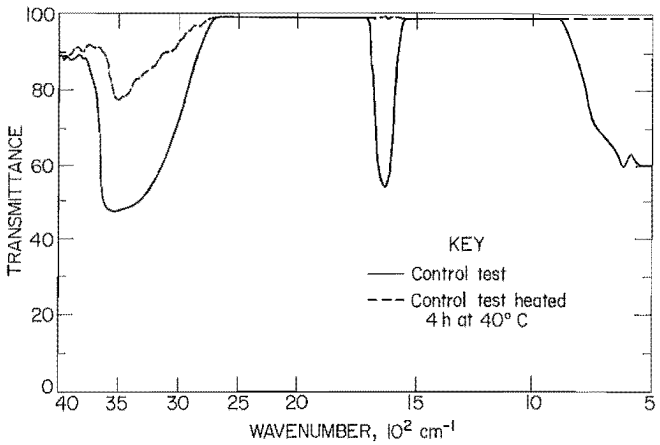

Figure 3.–IR spectra of ZnS precipitate before and after heating.

It is known that the removal of interlayer water from a material can be followed by IR spectroscopy (*4*). When interlayer water is removed, there is a decrease in the area under the curve associated with the water bending band. To investigate this phenomena, zinc sulfide was heated at 40° C for 4 h and the IR spectra taken. Zinc hydroxide and copper hydroxide were not studied in this way due to the relatively low thermal stability of these two hydroxide compounds. The results shown in figure 3 show a large decrease in the water bending band (1,612 cm^{-1}), the O-H stretching band (3,523 cm^{-1}), and the torsional oscillations bands (620 cm^{-1}). This verifies that a decrease in the water bending vibration indicates interlayer water being removed.

These decreases in the areas of the frequency bands describing water also appear in the test spectra of zinc hydroxide and copper hydroxide, as well as zinc sulfide, due to the addition of flocculants. Table 3 shows the area under the curve before and after flocculation for zinc sulfide, zinc hydroxide, and copper hydroxide. The data for flocculated zinc sulfide and zinc hydroxide shows there were large decreases in the areas of all three water bands when either nonionic or anionic PAM was added. PEO also showed decreases in the area of these water bands, but the results were not as striking. The data for flocculated copper hydroxide showed a decrease in the O-H stretching band areas for both types of PAM. However, the water bending band showed little change and the areas of the torsional oscillations band actually increased. These results indicated both polymers contributed to increasing the amount of interlayer water of copper hydroxide. However, the excess water did not have an effect on the overall performance of the polymers since the previous analysis of the O-H stretching band indicated an increased stability of the precipitate system via a water bridge. The increased stability seems to be conducive for the flocculation of copper hydroxide to occur despite the excess water. The PEO tests showed an increase in all three water band areas, which indicated PEO contributed to an increase in interlayer water of the copper hydroxide precipitate.

Table 3.–Area of frequency bands describing water for IR tests of ZnS, $Zn(OH)_2$, and $Cu(OH)_2$ precipitates, relative units

Precipitate and polymer	O-H stretching	H_2O bending	Torsional oscillations
ZnS:			
Control[1]	310	37	111
Nonionic PAM	71	13	9.2
Anionic PAM	104	9.6	0.3
PEO	185	4.6	4.9
$Zn(OH)_2$:			
Control[1]	188	23.1	39.4
Nonionic PAM	54	17.5	9.2
Anionic PAM	64	5.3	8.3
PEO	115	13.9	15.1
$Cu(OH)_2$:			
Control[1]	222	24.2	9.1
Nonionic PAM	194	23.9	19.0
Anionic PAM	176	22.3	15.7
PEO	249	32.5	15.2

[1]Precipitate without polymer.

A similarity can be seen between the dynamics of the frequency bands and the performance of the polymers. While preparing the samples for IR analysis, both types of PAM dewatered the zinc sulfide, zinc hydroxide, and copper hydroxide much better than PEO. PAM formed stronger flocs and dewatered the precipitate faster than PEO. The IR results reflected PAM's excellent ability and PEO's poor ability to dewater the three precipitates under investigation.

The next stage of the investigation was to study the possible shifts in the IR bands associated with the organic flocculating agents. The band shifts did not show up on the spectra at a polymer concentration of 0.075 g/L. To obtain a sharp spectra, the polymer's concentration had to be increased from 0.075 to 0.60 g/L. The test spectra were compared with the spectra of the polymers for group frequency band shifts due to the interactions with the metal precipitates (*10-11*). Table 4 lists the organic band assignments and the wave numbers at which they occur for each of the three polymers tested.

Table 4.–Organic group frequency band assignments of polymers and polymer-treated precipitates, wavenumbers

Polymer and band assignment	Polymer	Polymer treated	
		$Zn(OH)_2$	$Cu(OH)_2$
Nonionic PAM:			
C=O stretch	1,660	1,660	1,660
N-H deformation, C-N stretch	1,610	1,600	1,600
CH_2 deformation	1,450	1,450	1,450
Anionic PAM:			
C=O stretch	1,660	1,660	1,660
N-H deformation, C-N stretch	1,610	1,580	1,580
CH_2 deformation	1,450	1,450	1,450
Antisymmetric CO_2	1,560	1,560	1,560
Symmetric CO_2	1,410	1,410	1,410
PEO:			
CH_2 symmetric-antisymmetric	2,880	ND	2,880
	1,140	ND	1,140
C=O stretch	1,100	ND	1,100
	1,060	ND	1,060
CH_2 rock-twist	960	ND	960

ND Not determined.

Three bands dominated the spectra for the nonionic PAM-metal precipitate flocculation: carbonyl (C=O) stretch (1,660 cm^{-1}); N-H deformation, C-N stretch (1,610 cm^{-1}); and CH_2 deformation (1,450 cm^{-1}). The N-H deformation-C-N stretch showed a frequency band shift for both metal hydroxides. This is similar to the frequency shift described in the literature for metal-amine assignments in copper-urea complexes (*7*). Urea showed a shift in the C-N stretching frequency band upon complexation with copper to a lower frequency due to the formation of a stronger C-N single bond, thus indicating the coordination of copper through the nitrogen of the amine group. A similar interaction takes place between the amine group of the nonionic PAM and the metal hydroxide. The electron pair of the nitrogen atom, acting as a weak proton acceptor, is the most likely site of attachment. The C=O stretch showed no frequency band shift. Similar results have been reported for the copper complex of polyamide where no shift in the carbonyl frequency band was observed, thus, indicating the carbonyl group's lack of involvement in the bonding. Since no shift in the carbonyl frequency was observed for the metal hydroxide - PAM spectra, it can be assumed that carbonyl plays no role in the flocculation. A similar argument can be made for the CH_2 groups of the nonionic PAM since no shift was observed. The results of the anionic PAM test were very similar. The N-H deformation-C-N stretching vibration band shifted to a lower number indicating, again, the amide group is involved in the bonding. Two new bands appeared that were the antisymmetric CO_2 (1,560 cm^{-1}) and symmetric CO_2 (1,410 cm^{-1}). These frequencies are due to the carboxyl group. Neither frequency band showed a shift, indicating this group of the polymer is not involved in the bonding. As with nonionic PAM, the C=O stretch and the CH_2 deformation showed no band shift, indicating neither the carbonyl of the amide group nor the polymer chain is involved in the adsorption of the polymer.

Five group frequency bands dominated the spectra for PEO. They were CH_2 symmetric-antisymmetric (2,880 cm^{-1}), carbon-oxygen (C-O) stretch (1,140, 1,100, 1,060 cm^{-1}), and CH_2 rock-twist (960 cm^{-1}). These bands appeared in the spectra of the flocculated copper hydroxide, but it is unknown why the bands did not appear in the spectra of the zinc hydroxide tests. There is a shift in the 2,880 cm^{-1} band when PEO was adsorbed onto magnesium montmorillonite due to the CH_2 being sufficiently hydrophobic to adsorb onto the magnesium ion (*2*). However, for flocculated copper hydroxide, no band shift was observed. The spectra also showed that no band shift was observed for the CH_2 rock-twist band at 960 cm^{-1} and the C-O stretching bands. Although the analysis of the O-H stretching bands study indicates some interaction between polymer and precipitate, the lack of a frequency band shift indicates a very weak interaction. The interaction for PEO with the metal precipitate is probably through the ether oxygen similar to the nitrogen atom of the amide group on PAM. A more detailed investigation is required to confirm the role of PEO in this type of flocculation system.

CONCLUSIONS

The bonding of PAM and PEO on zinc and copper hydroxides was observed by studying the IR spectra of the flocculated precipitates. The spectra indicated bonding occurred at the nitrogen atom of PAM. The spectra also indicated the ether oxygen is the most likely site for bonding of PEO. The flocculant-metal precipitate matrix was stabilized by a water bridge for all polymers investigated. The spectra also showed a general decrease in the area of the three water bands, hydroxyl stretching, water bending, and torsional oscillations, indicating interlayer water was replaced during the flocculation sequence. However, during tests using PAM as the flocculant, a greater replacement of water was evident by the general decrease in area of water bands when compared with PEO flocculated material. This parallels observations that showed PAM as a superior flocculant over PEO for dewatering metal precipitates. This investigation shows how IR analysis can be instrumental in determining a flocculant's effectiveness for dewatering.

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